Electronic excitation of oriented molecules by low-energy electrons: An application to H_2

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We report inelastic differential cross sections for electronic excitation of an oriented molecule by low-energy electrons. Specifically we look at the dependence of these cross sections for the $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ transition in H_2 on both incident and scattered angles as well as on impact energy. These electron scattering cross sections exhibit a pronounced dependence on the incident and scattered angles, which suggests that related electron-energy-loss spectroscopy studies can be a useful probe of adsorbate-substrate structure.

I. INTRODUCTION

Electron-energy-loss spectroscopy (EELS) has emerged as, perhaps, the single most important tool for probing the properties of adsorbate molecules.[1–10] This spectroscopy can provide the vibrational frequencies and the energies of the electronically excited states, as well as the orientation of the adsorbed molecules with respect to the surface. While this technique has been widely used to study adsorbate vibrations, its usefulness in determining electronic excitation energies of adsorbate-substrate complexes has only recently been exploited.[11–13] Electronic excitations play an important role in many surface phenomena, such as electron-stimulated desorption, surface photochemical reactions, surface-enhanced photofragmentation, and surface-enhanced Raman scattering. Although there has been significant growth in the number and quality of experimental studies of vibrational EELS, the progress in related theoretical studies has been limited.[14–16] These theoretical studies have proved to be useful in the analysis and interpretation of the experimental data. However, to our knowledge no theoretical attempts to analyze the inelastic cross sections associated with the electronic excitation of oriented or adsorbed molecules have been reported.

The main objective of the present work is to report inelastic differential cross sections for electronic excitation of an oriented molecule by low-energy electrons. More specifically, we look at the cross sections for the $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ transition in oriented H_2. These electronic excitation cross sections will be seen to exhibit a pronounced dependence on the incident and scattered angles which can readily serve as a simple probe of adsorbate orientation. Even though H_2 is not a highly realistic prototype adsorbate system for studies of electronic EELS, we choose this transition because the $b^3\Sigma_u^+$ state is a valence-like triplet excited state, and valence triplet excited states will almost certainly be a feature of considerable interest in such studies.[13] For those features we seek to illustrate in these calculations the fact that this state is dissociative is not important. Furthermore, H_2 is a convenient small system and quantitatively reliable techniques are now available for studying these excitation cross sections in the gas phase.[17–21] In this very simple system the adsorbate-substrate interaction is completely ignored and the only role of the surface is to orient the molecule. Photoemission studies[22–24] have shown that isolated oriented molecules can serve as meaningful models of absorbates.

The outline of our paper is as follows. In Sec. II we present a brief review of the Schwinger multichannel theory which is the formulation we have used to obtain these electron impact excitation cross sections. In these calculations only the two open channels, i.e., the $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$ states, were included. Section III contains some relevant computational details and a discussion of our results. There we also include the elastic scattering cross sections for oriented H_2 which are of related interest and, moreover, can be compared with the results of an earlier study. In Sec. IV we summarize our conclusions and discuss the several directions in which studies of this type can be extended and made more realistic.

II. METHOD

The cross sections for electron impact excitation of oriented H_2 which we will present below have been obtained by the application of the Schwinger multichannel theory. The details of this theory have been discussed previously[20,25,26] and hence we will give only a brief review here. The formulation begins with a projected Lippmann-Schwinger equation

$$P\Psi_n^{(+)} = \frac{1}{\sqrt{N+1}} S_n + G_P^{(+)} V \Psi_n^{(+)} , \quad (1)$$

where $\Psi_n^{(+)}$ is the total $(N+1)$-particle wave function with plane-wave and outgoing-wave boundary conditions for the nth channel. The projection operator P defines the open-channel space in terms of the N-particle eigenfunctions of the target Hamiltonian H_N,

$$P=\sum_{m=1}^{\text{open}} |\Phi_m(1,2,\ldots,N)\rangle\langle\Phi_m(1,2,\ldots,N)| \tag{2}$$

and

$$H_N|\Phi_m\rangle=E_n|\Phi_m\rangle, \quad E-E_m>0 \tag{3}$$

where E is the total energy of the $(N+1)$-particle system. In Eq. (1) S_n is the free-particle solution of the unperturbed Hamiltonian $H_0=H_N+T_{N+1}$ and is given by

$$S_n=\Phi_n e^{i\mathbf{k}_n\cdot\mathbf{r}_{N+1}} . \tag{4}$$

The interaction potential V between the incident electron and the target molecule is

$$V=H_{N+1}-H_0=\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_{N+1}|}-\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{R}_\alpha-\mathbf{r}_{N+1}|} , \tag{5}$$

where the first and second terms of Eq. (5) represent electron-electron and electron-nuclei interaction, respectively. The outgoing-wave Green's function $G_P^{(+)}$, defined only in the open-channel space, can be written as

$$G_P^{(+)}=\sum_{m=1}^{\text{open}} |\Phi_m\rangle g_m^{(+)}(\mathbf{r}_{N+1},\mathbf{r}'_{N+1})\langle\Phi_m| \tag{6}$$

with

$$g_m^{(+)}(\mathbf{r},\mathbf{r}')=-\frac{1}{2\pi}\frac{e^{ik_m|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} . \tag{7}$$

A complete equation for $\Psi_n^{(+)}$ including the unprojected component of Eq. (1) can be written as[26]

$$\left[\tfrac{1}{2}(PV+VP)-VG_P^{(+)}V+\frac{1}{N+1}\left[\hat{H}-\frac{N+1}{2}(P\hat{H}+\hat{H}P)\right]\right]\Psi_n^{(+)}=\frac{1}{\sqrt{N+1}}VS_n , \tag{8}$$

where $\hat{H}=E-H_{N+1}$. This equation contains information about the closed channels without defining the closed-channel Green's function which, in turn, would require the inclusion of the target continuum states.[27] Based on Eq. (8) a variational functional for the fixed-nuclei scattering amplitude is

$$f^B(\mathbf{k}_m,\mathbf{k}_n)=-\frac{1}{2\pi}\frac{\langle S_m|V|\Psi_n^{(+)}\rangle\langle\Psi_m^{(-)}|V|S_n\rangle}{\left\langle\Psi_m^{(-)}\left|\tfrac{1}{2}(PV+VP)-VG_P^{(+)}V+\frac{1}{N+1}\left[\hat{H}-\frac{N+1}{2}(P\hat{H}+\hat{H}P)\right]\right|\Psi_n^{(+)}\right\rangle} . \tag{9}$$

$f^B(\mathbf{k}_m,\mathbf{k}_n)$ is the full scattering amplitude calculated in the molecular frame.

In our procedure trial scattering wave functions $\tilde{\Psi}_n^{(+)}$ are expanded in a basis of $(N+1)$-particle Slater determinants which are constructed from an orthogonal set of molecular self-consistent-field (SCF) orbitals augmented by additional basis functions. These additional basis functions may be needed to adequately represent the scattering orbitals. This augmented basis is further expanded in Cartesian Gaussian functions. With this choice of basis all the matrix elements arising in Eq. (9), except for those of $VG_P^{(+)}V$, can be evaluated analytically for molecules of arbitrary geometry. Furthermore, the matrix elements of $VG_P^{(+)}V$ can also be obtained analytically by a quadrature-like insertion of a large Cartesian Gaussian basis around $G_P^{(+)}$.[28–30] Although this insertion quadrature must be used for the principal-value contribution of this term, the residue contribution can actually be obtained exactly.[31]

This formulation directly provides an analytical approximation to the body-frame full scattering amplitude, $f^B(\mathbf{k}_m,\mathbf{k}_n)$, for a molecule in some fixed orientation and of arbitrary geometry. The incident and scattered angles are specified in $\mathbf{k}_n$ and $\mathbf{k}_m$. In contrast to gas-phase collisions, where a frame transformation and orientational averaging are physically required, for oriented molecules $f^B(\mathbf{k}_m,\mathbf{k}_n)$ gives the observed differential cross sections directly.

III. PROCEDURES AND RESULTS

In this section we present the first results for the cross sections for electronic excitation of an oriented molecule by low-energy electrons. Specifically we report differential cross sections for the $X^1\Sigma_g^+\rightarrow b^3\Sigma_u^+$ excitation of H_2 by electrons with impact energies of 12, 15, and 25 eV. We also show the elastic differential cross sections for oriented H_2 for incident energies around the broad shape resonance feature.[32]

For the initial state ($X^1\Sigma_g^+$) in this electronic excitation we use an SCF wave function obtained with the uncontracted $(6s4p)$ Cartesian Gaussian basis shown in Table I. At the internuclear distance of $1.4003a_0$ the SCF energy was found to be $-1.133\,232$ a.u. For the $b^3\Sigma_u^+(1\sigma_g 1\sigma_u)$ excited state we make a frozen-core approximation and determine the $1\sigma_u$ orbital by diagonalizing the V_{N-1} potential of the core in the SCF basis. Our resulting fixed-nuclei vertical excitation energy for the $X^1\Sigma_g^+\rightarrow b^3\Sigma_u^+$

TABLE I. Cartesian Gaussian basis sets. Cartesian Gaussian function defined by $X_{lmn}=N_{lmn}(x-A_x)^l(y-A_y)^m(z-A_z)^n \times\exp(-\alpha|\mathbf{r}-\mathbf{A}|^2)$. Quadrature basis used in evaluating $\langle\tilde{\Psi}_m|VG_P^{(+)}V|\tilde{\Psi}_n\rangle$ (see text).

Center and type	Exponent
H, $6s$[a]	48.4479, 7.283 46, 1.651 39, 0.462 447, 0.145 885, 0.07
H, $4p$[a]	1.50, 0.50, 0.25, 0.125
Midpoint, $5s$	1.0, 0.5, 0.25, 0.0625
Midpoint, $5p$	1.0, 0.5, 0.25, 0.125, 0.0625

[a] Used in SCF and scattering basis. The basis includes P_x, P_y, and P_z functions.

transition was 9.99 eV. This is the value we assumed as a threshold energy. The scattering orbitals in the trial wave functions $\tilde{\Psi}_n$ and $\tilde{\Psi}_m$ of Eq. (9) were expanded in the basis of the virtual orbitals of the SCF calculation carried out with the basis of Table I. In the body frame all calculated amplitudes include the Σ_g, Σ_u, Π_g, and Π_u symmetries of the $(N+1)$-particle functions, $\tilde{\Psi}_n$ and $\tilde{\Psi}_m$. The basis for the quadrature-like insertion used to evaluate the

$$\langle\tilde{\Psi}_m^{(-)}|VG_P^{(+)}V|\tilde{\Psi}_n^{(+)}\rangle$$

matrix element in Eq. (9) consists of the SCF basis set augmented by additional functions at the center of the molecule. At each incident energy the differential cross sections are obtained from a fixed-nuclei calculation.

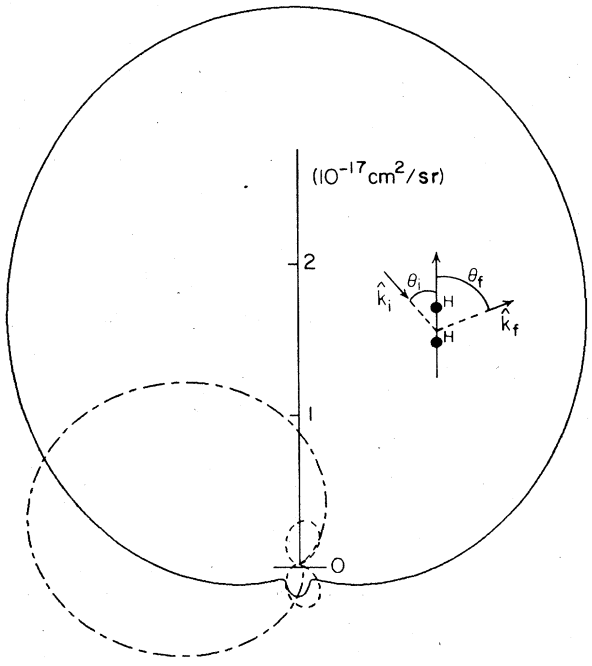

FIG. 1. Polar plots of the differential cross sections (10^{-17} cm^2/sr) for the electronic excitation of the $b^3\Sigma_u^+$ state of oriented H_2 at 12 eV, for incident angles of 0°, 45°, and 90°. The scattering geometry is shown in the inset. ——, $\theta_i=0°$; – – –, $\theta_i=45°$; ------, $\theta_i=90°$.

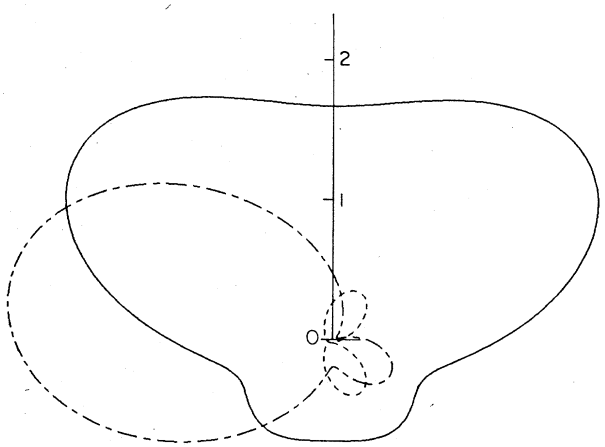

FIG. 2. Polar plots of the differential cross sections for the electronic excitation of the $b^3\Sigma_u^+$ state of oriented H_2 at 15 eV. Same incident angles, scattering geometry, and units as in Fig. 1. ——, $\theta_i=0°$; – – –, $\theta_i=45°$; ------, $\theta_i=90°$.

This corresponds to making the Franck-Condon[33] approximation and summing over the entire band system.

To begin, we consider the molecule to be oriented perpendicular to an assumed surface. Moreover, we choose the incident and scattered electrons to be in the same plane. Figures 1–3 show polar plots of the differential cross sections for excitation of the $b^3\Sigma_u^+$ state of H_2 by electrons with incident energies of 12, 15, and 25 eV, respectively. Each figure gives the cross sections as a function of scattered-electron angle for incident directions of 0°, 45°, and 90°, where all angles are measured relative to the molecular axis which, in this case, coincides with

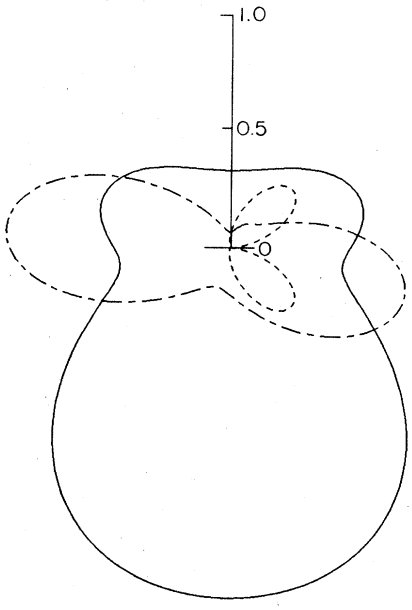

FIG. 3. Polar plots of the differential cross sections for the electronic excitation of the $b^3\Sigma_u^+$ state of oriented H_2 at 25 eV. Same incident angles, scattering geometry and units as in Fig. 1. ——, $\theta_i=0°$; – – –, $\theta_i=45°$; ------, $\theta_i=90°$.

the normal to the surface. These differential cross sections show characteristic angular distributions which depend strongly on both the energy and the direction of the incident and scattered electron beam. For example, at normal incidence ($\hat{\mathbf{k}}_i = \mathbf{0}$) and for lower impact energies the cross sections are strongly backward peaked, as expected.[34] This feature is due to the exchange nature of the excitation mechanism and is well known in gas-phase collisions. This behavior will characterize cross sections for singlet-triplet or other spin-forbidden optical transition. As the incident energy increases, the forward scattering becomes more apparent. Moreover, for a given energy the excitation cross section decreases markedly as the direction of the incident electron changes from normal to 90°. This feature is a consequence of the symmetry of the electronic states involved in the transition. Clearly the dependence of these cross sections both on energy and angles can be a very useful probe of adsorbate-substrate geometry.

For the next example we consider the excitation of an oriented molecule tilted with respect to the normal. Vibrational EELS has already proved useful in studies of tilted adsorbates.[35] For many systems measured electron-energy-loss spectra would generally correspond to an unweighted orientational average of the differential cross sections around the normal on a cone of angle β. To obtain these orientationally averaged cross sections in the laboratory frame (normal to the surface) for many incident directions, it is convenient to work with a partial-wave representation of the scattering amplitude, i.e.,

$$f^B(\mathbf{k}_m,\mathbf{k}_n)=\sum_{\substack{l,\bar{m},\\ l',m'}} f_{l\bar{m}}^{l'm'} Y_l^{\bar{m}}(\hat{\mathbf{k}}_m) Y_{l'}^{m'*}(\hat{\mathbf{k}}_n)\ , \tag{10}$$

where $f_{l\bar{m}}^{l'm'}$ is given by

$$f_{l\bar{m}}^{l'm'}=\int f^B(\mathbf{k}_m,\mathbf{k}_n) Y_l^{\bar{m}*}(\hat{\mathbf{k}}_m) Y_{l'}^{m'}(\hat{\mathbf{k}}_n) d\Omega_{\hat{\mathbf{k}}_m} d\Omega_{\hat{\mathbf{k}}_n}\ . \tag{11}$$

In the partial-wave expansion of the scattering amplitude, Eq. (10), we included terms with $l \le 4$. An N-point Gauss-Legendre quadrature is used to carry out the integrations in Eq. (11). This requires that $f^B(\mathbf{k}_m,\mathbf{k}_n)$ be determined at the appropriate set of angles. The laboratory-frame scattering amplitude can then be straightforwardly written as

$$f^L(\mathbf{k}'_m,\mathbf{k}'_n)=\sum_{\substack{l,\bar{m},\mu\\ l',m',\mu'}} f_{l\bar{m}}^{l'm'} D_{\mu\bar{m}}^{(l)}(\omega)[D_{\mu'm'}^{(l')}(\omega)]^* \times Y_l^{\mu}(\hat{\mathbf{k}}'_m) Y_{l'}^{\mu'}(\hat{\mathbf{k}}'_n)\ , \tag{12}$$

where the primed coordinates refer to angles in the laboratory frame and $\mathbf{D}$ is the rotation matrix whose argument consists of the Euler angles (α,β,γ) specifying the orientation of the molecule in the laboratory frame. For a linear molecule the average of the differential cross section determined by Eq. (12) over the angle γ is meaningless. However, this differential cross section averaged over α, $\langle d\sigma/d\Omega \rangle$, is given for an angle of tilt β by

$$\left\langle \frac{d\sigma}{d\Omega} \right\rangle = \sum_{L,L',M} \beta_{LM,L'-M} Y_L^M(\hat{\mathbf{k}}'_m) Y_{L'}^{-M*}(\hat{\mathbf{k}}'_n)\ , \tag{13}$$

with

$$\beta_{LM,L'-M}=\left[\frac{(2L+1)(2L'+1)}{4\pi}\right]^{1/2} \sum_{\substack{l,m,l_1,m_1,\\ l',m',l'_1,m'_1,J}} (-1)^{m_1+m'} \times[(2l+1)(2l_1+1)(2l'+1)(2l'_1+1)(2J+1)]^{1/2} \times f_{lm}^{l'm'}(f_{l_1m_1}^{l'_1m'_1})^* \begin{bmatrix} l & l & L \\ m & -m_1 & m_1-m \end{bmatrix} \begin{bmatrix} l' & l'_1 & L' \\ -m' & m'_1 & m'-m'_1 \end{bmatrix} \times \begin{bmatrix} l & l_1 & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l' & l'_1 & L' \\ 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} L & L' & J \\ -M & M & 0 \end{bmatrix} \begin{bmatrix} L & L' & J \\ m-m_1 & m'_1-m' & 0 \end{bmatrix} Y_J^0(-\beta)\delta_{m_1-m,m'_1-m'}\ . \tag{14}$$

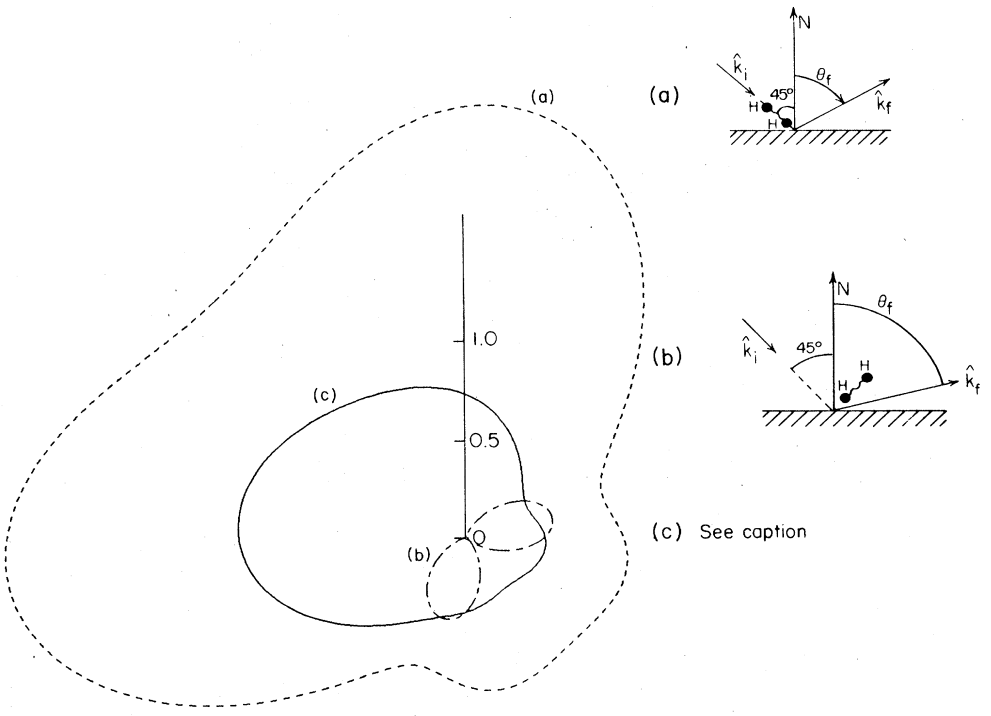

FIG. 4. (a) Differential cross sections for excitation of the $b^3\Sigma_u^+$ state of an oriented H_2 molecule with tilt angle of 135°. The angle of incidence is shown in the inset ("head-on" collision). (b) Differential cross sections for excitation of the $b^3\Sigma_u^+$ state of an oriented H_2 molecule with tilt angle of 45°. The angle of incidence is shown in the inset ("perpendicular" collision). (c) Differential cross sections for excitation of an oriented H_2 molecule averaged over a cone of angle 45°. Angle of incidence as in insets (a) and (b). Same units as in Fig. 1.

Figure 4 shows a polar plot of the cross section for excitation of a molecule averaged over a cone of angle β by electrons incident at 45° and with kinetic energy of 15 eV. It is important to note that this averaging includes orientations for which the cross sections are markedly different. To illustrate this effect we also show in the same figure and for the same angle of incidence, $\hat{\mathbf{k}}_i$, cross sections for excitation of a fixed molecule with tilt angles of 45° and 135°, i.e., a "perpendicular" and "head-on" collision, respectively. This orientational averaging is clearly an important effect.

For the purpose of comparison we have also studied the cross sections for elastic scattering of electrons by H_2 oriented normal to an assumed surface. Davenport *et al.*[15] have previously studied these elastic cross sections for H_2, N_2, and CO using a continuum multiple-scattering formalism. Our cross sections were obtained starting from the results of previous calculations of gas-phase collisions at energies where polarization effects are known to be important.[25] These effects were taken into account through the inclusion of closed channels in the expansion of the scattering wave function in the Schwinger multichannel formulation. Actually, such polarization effects can almost certainly be masked by adsorbate-substrate interactions. Details of these calculations including the basis-set expansions used have been given elsewhere.[25] In Fig. 5 we show our calculated elastic cross sections for 4-eV electrons incident at 45° along with the only other available results of Davenport *et al.* Our calculated cross

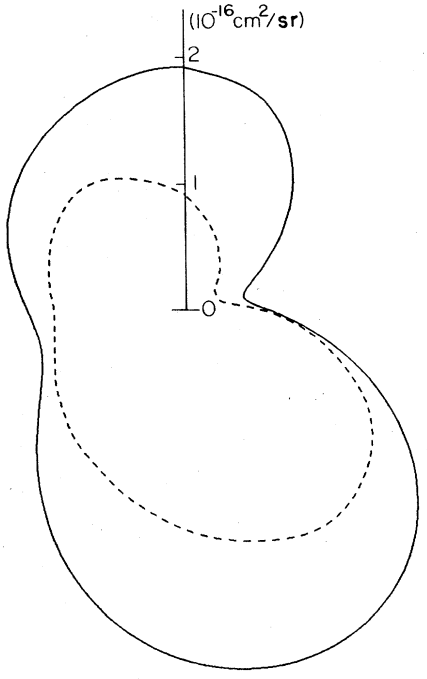

FIG. 5. Polar plots of elastic differential cross sections for e-oriented H_2 scattering at 4 eV. The incident angle is 45°. Solid lines, present results; dashed lines, results from Fig. 7(a) of Ref. 15. Same scattering geometry as in Fig. 1.

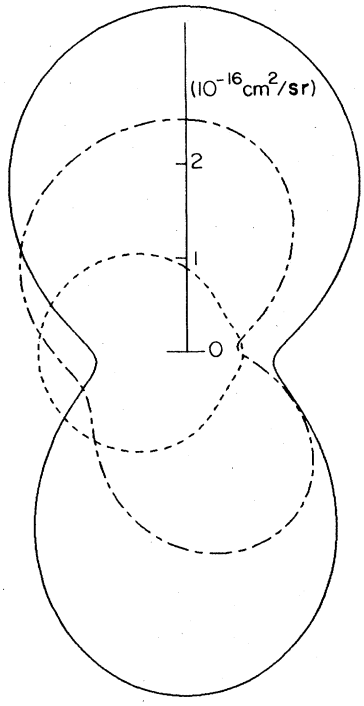

FIG. 6. Polar plots of elastic differential cross sections for e-oriented H_2 scattering at 3 eV, for incident angles of 0°, 45°, and 90°. Same scattering geometry as in Fig. 1. ——, $\theta_i=0$; — — —, $\theta_i=45°$; ------, $\theta_i=90°$.

sections are certainly in qualitative agreement with those of Davenport *et al.*[15] Figure 6 shows the elastic cross sections for 3-eV electrons at 0°, 45°, and 90° incidence for normal H_2. These cross sections display an obvious dependence in shape and magnitude on the direction of incidence. The p-wave character of the well-known shape resonance is also very apparent for the "head-on" collision. These elastic fixed-nuclei scattering amplitudes are required in studies of vibrational excitation of adsorbate molecules by low-energy electrons.[15] Work along these lines is underway.

IV. CONCLUDING REMARKS

In this paper we have studied the cross sections for electronic excitation of oriented H_2 molecules by low-energy electrons. These cross sections exhibit a strong dependence on both incident- and scattered-electron angles and on impact energies which could be used as a powerful probe of adsorbate-substrate structure. Although the hydrogen molecule is not an interesting surface adsorbate, the energy and angular dependencies of the cross sections for excitation of the valence-like $b\,^3\Sigma_u^+$ state studied here can be expected to be characteristic of the related behavior of more realistic adsorbates such as CO and N_2. The symmetries of the electronic orbitals involved in the excitation will also undoubtedly influence the angular patterns observed in such electronic EELS experiments. The present results suggest that it is worthwhile to extend these preliminary studies beyond this simplified model of an isolated oriented molecule. For example, the adsorbate-substrate interaction can be partly simulated by a local-cluster model in which small clusters of atoms represent the substrate. Studies of the bonding of adsorbates have shown that such cluster models can be quite realistic.[36] The multichannel collision formulation employed here is also applicable to electron-impact excitation of molecules adsorbed on these small-cluster models in both linear and nonlinear configurations.[37] Furthermore, other solid-state effects can be incorporated phenomenologically.

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